REFORMATION OF INORGANIC PARTICULATES SUSPENDED IN COAL-
DERIVED LIQUIDS AND IMPROVED SEPARATION*

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For coal liquefaction processes, the separation of fine inorganic
particulates from the organic product matrix represents an important tech-
nical problem. This problem is difficult because the matrix is viscous and
many of the particles are in the micron and submicron size range, Separation
methods and devices tried with some success in separating the particles have
been: hydroclones, centrifugation, magnetic separation, solvent extraction,
solvent fractionation, and filtration. These techniques suffer, however, in
varying degrees from unsatisfactory operation, maintenance, throughput, and
cost. To help correct these shortcomings, we have undertaken a study of
techniques by which the fine particulates might be enlarged or better
collected. Some progress toward that end has been described in the open
and patent literature for solvent addition. In these works, two mechanisms
by which solvent improves separation have been suggested: (1) the solvent
may soften or dissolve a coating from the particles, permitting physical
attractive forces to cause agglomeration; or (2) the solvent may cause
phase separation--the heavier phase acting as a collection flocculant.

This paper consists of five parts. First, I will describe the labora-
tory sedimentation test used in this study. Second, I will discuss the
effects of solvent dilution on settling. Our main thrust will come in
parts three and four, where settling with heating and with the addition of
chemical promoters will be presented. These areas have not (to our
knowledge) been studied previously. In part five, I will describe the
possible mechanisms and the roles that each may play.

The laboratory sedimentation tests were conducted in a vertical 18-
inch-tall by 1-inch-diameter metal tube using unfiltered oil from the
Solvent Refined Coal process. Normally,175 grams of this oil containing
suspended particles was placed in the tube. The sealed tube was quickly
heated to test temperature and then cooled rapidly at the end of the test.
The contents, as shown in slide 1, were then separated into 10 or 11
fractions for examination by filtration, microscopy, or chemical analysis.
The filtration was achieved by the use of a laboratory technique that I
have described in the July 1976 issue of I&EC Process Design and Development.

The sedimentation tests with solvent dilution, using toluene or SRC
recycle solvent as the diluent, gave comparable results with appreciable

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improvement in settling at 20% dilution. In slide 2, data are shown for
settling at 310°C for 1 hour with 5, 10, and 20% dilution with recycle
solvent; the ash for the 20% dilution is approaching the EPA requirement
of 0.15% in the top 70% of the sedimentation tube. The role of particle
agglomeration appears well-substantiated here since the agglomerates
formed can be observed by optical microscopy to contain as many as 100
of the particles. Calculations of effective particle size from the
settling rates indicate that the settling particles are a minimum of
53 microns in diameter whereas 90% of the particles in the starting
test are less than 1 micron in diameter.

Keeping in mind that with 20% solvent dilution, adequate clarity
can be approached by settling for 1 hour at 310°C, let us turn to part
two. What can be done with heat alone? In slide 3, data are plotted
that represent the results of a series of sedimentation tests conducted
at temperatures of 100 to 350°C and for times of 1 to 21 hours. The
filtration improvement factor is a term describing the relative filter-
ability of the third fraction from the top; a factor of 1 is no
improvement, whereas a factor of 20 or more indicates clarity meeting
EPA standards. Little settling was found after 18 hours at 100 and
150°C. At 200 and 250°C, settling was more rapid and clarity was
reached before 18 hours. At 310°C in 3 hours and at 350°C in 1 hour,
the results were good. At higher temperatures, settling was poor be-
cause of decomposition. Therefore, 300 to 350°C appears to be the best
working range. Settling at 350°C seems at least as good as with 20%
solvent dilution at 310°C. The effects upon the particles may be
considerably different since both the size and distribution of particles
apparently change upon thermal treatment. Slide 4 shows particles in
the starting oil at 24,000 magnification. Some of the particles are
only 0.01 micron in diameter; the larger particles are rough on the
edges, which suggests that they may be composed of smaller particles.
Slide 5 reveals a similar magnification of the particles after treatment
at 300°C for 1 hour; few particles less than 1 micron in size remain
and the surface edges appear to be smooth.

With evidence that significant changes in particle size and form occur
during a 1-hour thermal treatment, it follows that, during that treatment,
the rate of transport of particles or their components must be appre-
ciable and that the transport rate might usefully be increased by changing
the system properties. We limit considerations here to additions of
promoters in such small quantities that their economic recovery may not
be required. Such candidate promoters were selected from two different
groups: (1) organic materials which had previously been used to change
properties of colloids and suspensions and (2) inorganic materials
(particularly inexpensive ones) which could change the charge or chemical
form of the particle surface. Initial scouting tests were made with
4,000 ppm of the additive for 70 minutes or less at 280°C. Additional
testing at other conditions followed in cases where positive improvement
was found.

Of the 34 organic and 25 inorganic candidate materials tested, four
organic and nine inorganic appear to give some improvement. The best
organic additive tested was Tretolite sample 771-119; at concentrations

of 4,000, 2,000, or 500 ppm, the ash found in the top fraction was less
than 0.05%, which represented results that were 5 times better than
control tests. Three other organic additives supplied by Tretolite
Division of the Petrolite Corporation of St. Louis, Missouri, appeared
to cause lesser improvement. The next slide shows the results of three
pairs of sedimentation tests using the 771-119 additive at 4,000 ppm.
The control was run before each additive test, with the six tests being
made in a single sequence to minimize experimental variations. Signi-
ficantly lower ash contents are noted for fractions 1 through 7 for the
additive tests; larger ash contents are shown for the bottom fraction
(as expected).

     For the three additive tests, the ash content in the first 3
fractions was low, gradually increasing up to the 7th fraction and then
sharply rising thereafter. Two of these runs were for 48 minutes, and
1 run was for 30 minutes. These figures include the time required for
bringing the sample to test conditions; therefore, the actual operating
time was less than the times shown. Each fraction represents about
3.5 cm in depth; thus, the settling rate for the smallest particle
appears to be about 20 cm (or nearly 8 inches per hour).

     Of the inorganic additives selected, aluminum sulfate, ammonium
sulfate, and ammonium hydrogen sulfate appeared as effective as any
organic additive tested. Aluminum phosphate appeared to perform better
at temperatures near 340°C, while ammonium monohydrogen phosphate seemed
to be less effective. Phosphoric acid, phosphoric anhydride, and sul-
furic acid appeared to be most effective at higher concentrations such
as 10,000 ppm but also seemed to be effective at temperatures as low as
200°C--phase separation in the matrix material and possibly flocculation
were noted even at this low temperature.

     These laboratory data indicate that, through heat treatment in the
presence of a small amount of a promoter, settling takes place in less
than 1 hour and, therefore, does meet clarity standards. Other arrange-
ments, such as to couple settling with a polishing step, may be useful.
The effect of heat upon settling has been confirmed in a larger-scale
system, and the effect of additives is still being studied. These
results will be reported at a later date.

     Turning now to another consideration, the next slide tabulates
some possible mechanisms which may promote settling. Since a wide range
of particle types and compositions exist in a suspension in a variable
matrix, several settling mechanisms may be operating simultaneously.
Agglomeration is known to occur both after solvent dilution and upon the
application of heat. The extent to which charge, melting, or chemical
conversion occurs to promote agglomeration has not yet been established.
Electron-microscope studies of before and after heat treatment indicate
that particle reformation does occur. It implies some solubility of
the organic species in the matrix organic materials at the test condi-
tions, which is not particularly surprising in view of the polar
components of the organic matrix. None of the promoters, when used
alone, appear to flocculate and gather up particles as we would expect
to observe in aqueous systems; however, some of the additive tests,

particularly those with phosphoric acid, phosphoric anhydride, and
sulfuric acid seem to cause a small amount of a matrix phase to separate
out and collect particulates. The normal changes in viscosity that
are induced by temperature or by dilution with solvent are significant
but do not account for the measured settling rates. Phase separations,
as a result of treatment, can affect viscosity and, subsequently, the
settling rates.
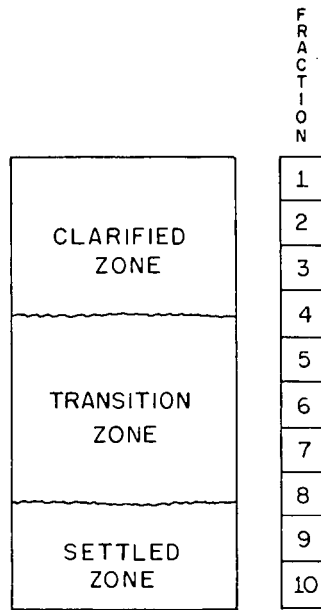
Generally: 1. Clarified zone contains particles less than 5 μ and has a
total solids concentration much less than the UFO.

2. Transition zone contains a few particles up to 15 μ and varies
from a low concentration to that of the UFO.

3. Settled zone contains nearly all large dark particles and
has a concentration much greater than UFO.

Fig. 1   Settling zone identification.

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ANALYTICAL RESULTS FOR SETTLING OF PROCESS RECYCLE DILUTED,
UNFILTERED OIL FROM THE SRC PROCESS

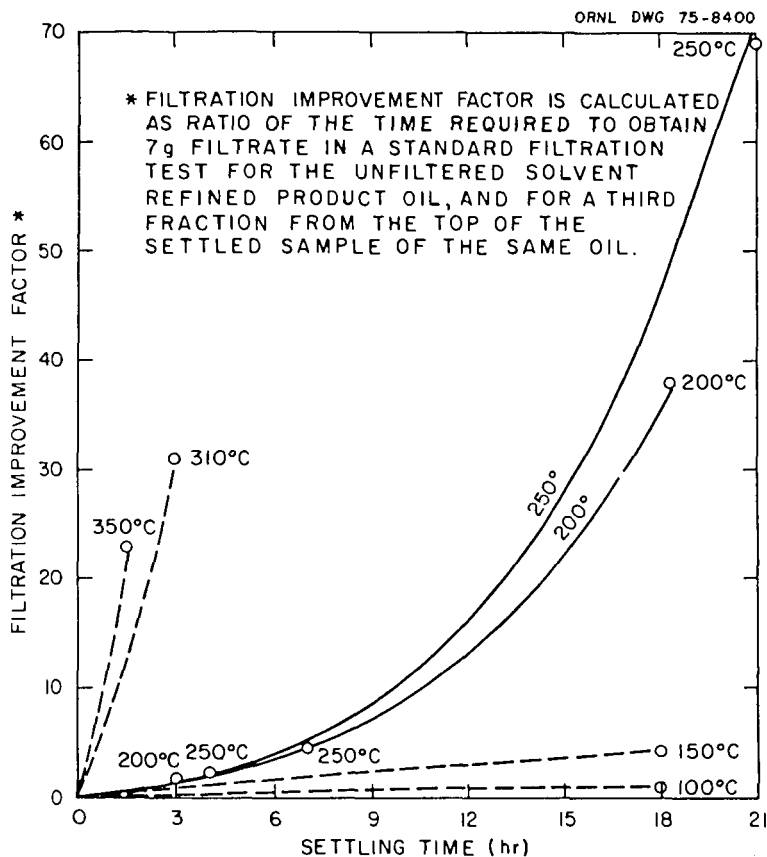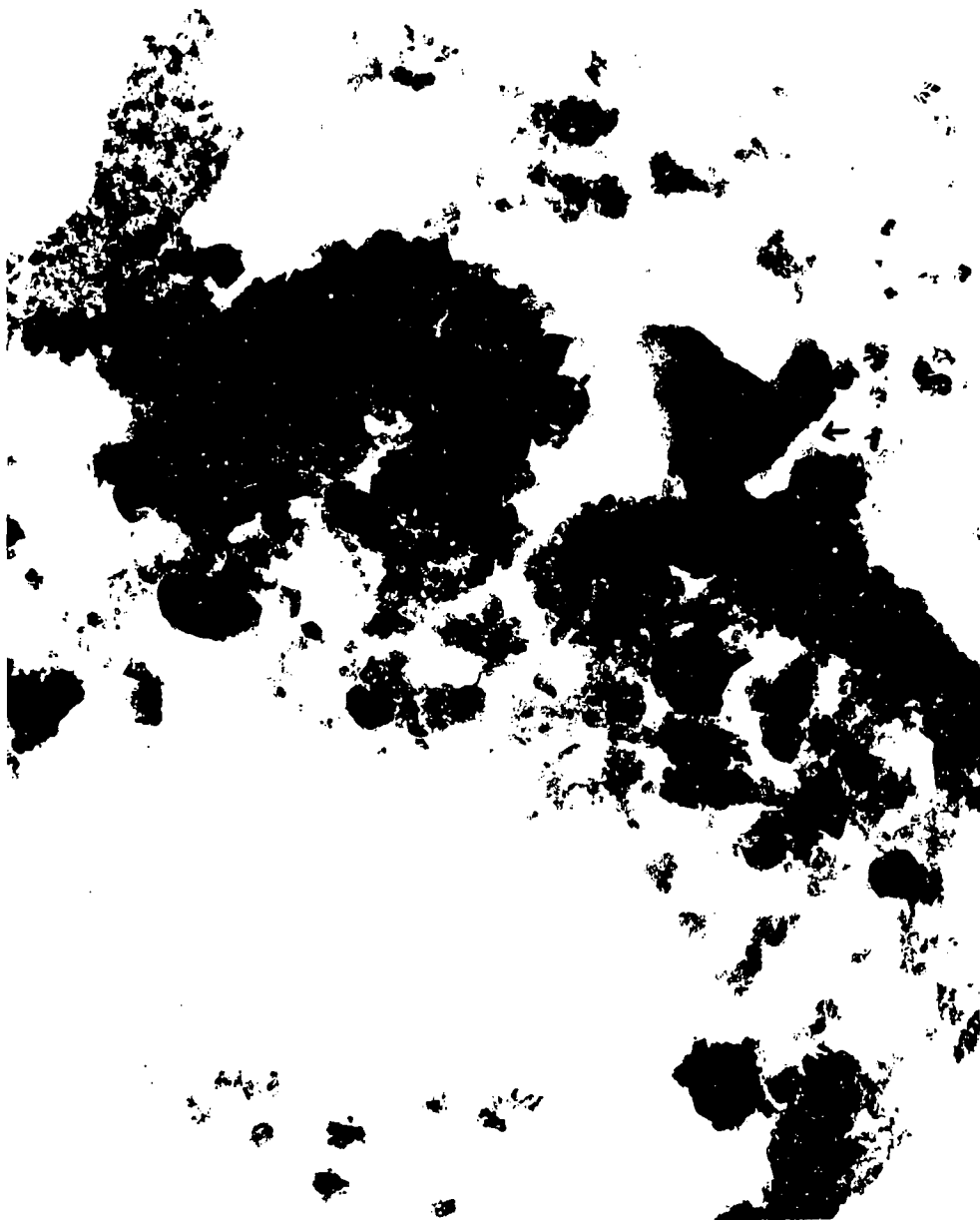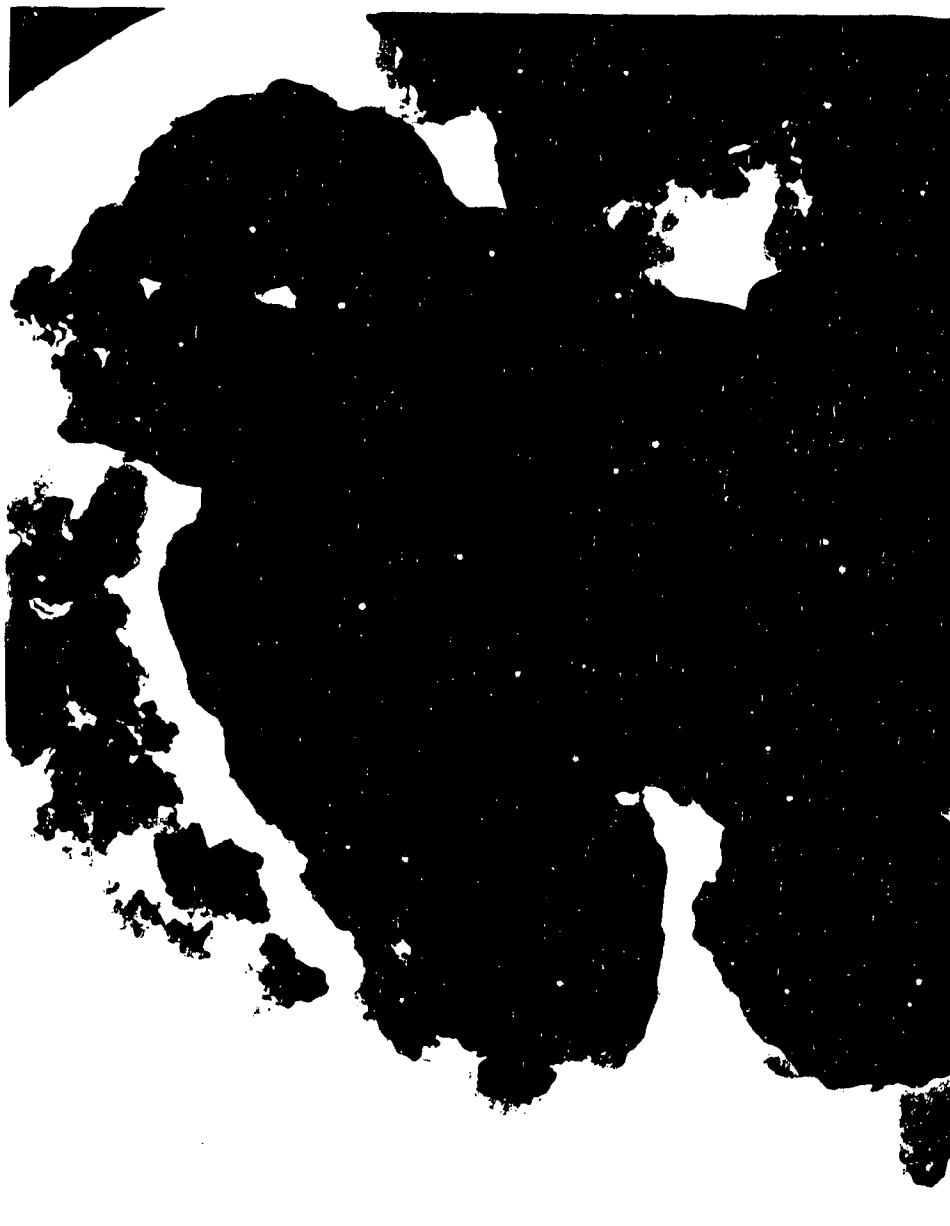| CONDITION	FRACTION NO.	ASH (WT %)	SULFUR (WT %)
1 HR AT 310°C, 5% DILUTION	1	1.67	0.63
	4	1.52	0.70
	7	1.44	0.67
	11	3.32	0.70
1 HR AT 310°C, 10% DILUTION	1	1.12	0.59
	4	0.72	0.60
	7	1.22	0.67
	10	3.49	0.75
1 HR AT 310°C, 20% DILUTION	1	0.33	0.50
	4	0.24	0.54
	7	0.03	0.54

Fig. 3. Improvement in filterability as a function of settling time and temperature.

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24,000 X   UNFILTERED SRC OIL |0.4μ|

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24,000 X   HEAT TREATED UNFILTERED SRC OIL   0.4μ

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30 min. AT
340 - 380 °C

3 RUNS WITH
4000 ppm
ADDITIVE

48 min. AT
280 - 315°C

3 CONTROL RUNS

48 min. AT 250 - 315°C

% ASH

TEST FRACTION
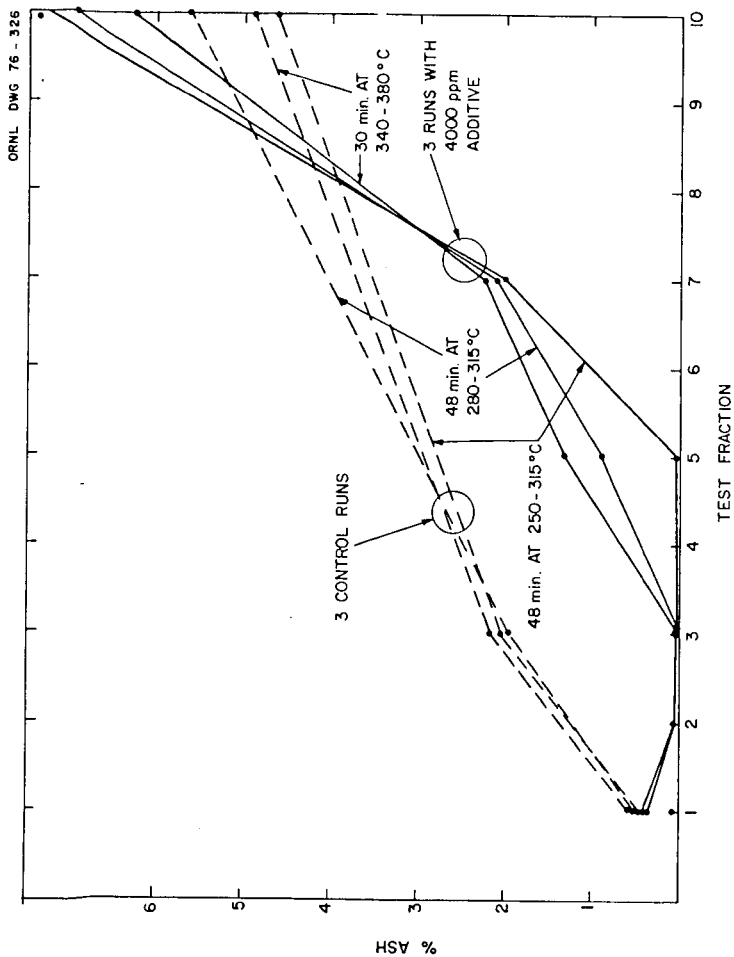
COMPARATIVE SETTLING TESTS

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POSSIBLE EVENTS LEADING TO MORE RAPID SETTLING

INITIAL EVENTS

NEUTRALIZATION OF ZETA POTENTIAL

MELTING AWAY OF HARD ORGANIC SURFACE LAYER

CHEMICAL CONVERSION OF SURFACE

PHASE SEPARATION

FINAL EVENTS

AGGLOMERATION

PARTICLE ENLARGEMENT THROUGH RECRYSTALLIZATION

FLOCCULATION

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